ELECTRON LOCALIZATION EFFECT ON THE EDGE-STATE MAGNETISM OF DISORDERED NETWORK OF NANOGRAPHENE SHEETS

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Introduction

The shape of a nanographene sheet is described in terms of a combination of armchair and zigzag edges. According to previous works [1-4], spin-polarized nonbonding π-electron state (edge-state) is formed in the zigzag edge region in spite of the absence of such state in armchair edges. The presence of edge-state spins therefore results in a variety of magnetism in nanographene, depending on its shape.

According to theoretical studies [2], the edge-state spins are strongly coupled in parallel with each other in a zigzag edge through strong intra-zigzag-edge ferromagnetic interaction J_0 having a strength of ~10^3 K. In a nanographene sheet with zigzag edge regions separated by the presence of armchair edges, the ferromagnetically coupled edge-state spins in a zigzag edge interact with those in other zigzag edge through inter-zigzag-edge ferromagnetic/antiferromagnetic interaction J_1 having a strength of ~ $(10^{-1} - 10^{-2})J_0$ and mediated by conduction π-carriers, where the strength and sign of J_1 depend on the mutual structural relation between the zigzag edges. Therefore, an arbitrary shaped nanographene sheet is expected to have a ferrimagnetic structure having a non-zero net ferrimagnetic moment as a consequence of a compensation of the constituent spins coupled by J_0 and J_1. In addition, the negligible magnetic anisotropy associated with a small spin-orbit interaction of carbon [5] gives a feature of isotropic Heisenberg spins.

Activated carbon fiber (ACF) [6,7] consists of a 3D disordered network of nanographite domains, each of which is a loose stack of 3 - 4 nanographene sheets with a mean in-plane size of 2 - 3 nm. Here, two kinds of extra interactions should be added due to its hierarchical structure; weak inter-nanographene-sheet antiferromagnetic interaction J_2, and inter-nanographite-domain antiferromagnetic one J_3. J_3 originates from the inter-nanographite-domain hopping integral and is in the range of several K. Since the electron transport in nanographene network is governed by the Coulomb-gap-type variable range hopping [7], strong electron localization is expected at lower temperatures, which in turn can affect the magnetism. Therefore, the magnetism of the edge-state spin system in the nanographene network are of particular interest in relation to the electron localization phenomenon.

In this paper, we show the electron-localization-induced inhomogeneous magnetic state of the edge-state spins in the networked nanographene sheets from ESR, static magnetic susceptibility

Results and Discussion

The temperature dependence of the ESR intensity and peak-to-peak width (ΔH_{PP}) in vacuum at microwave powers of 1 and 10 μW are given in Figs. 1(a) and (b), respectively. The intensity at 1 μW obeys the Curie law down to 30 K, and

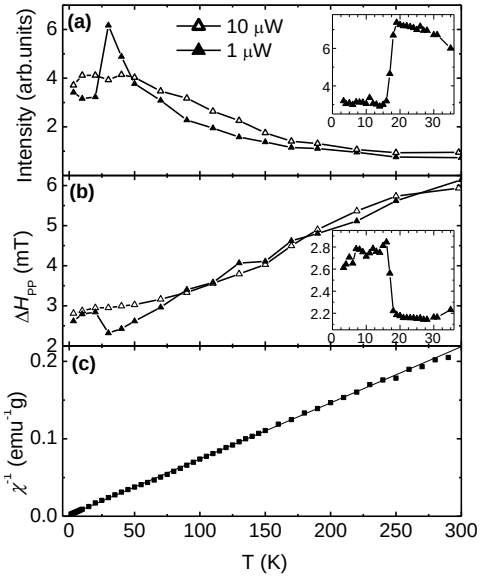

Figure 1. (a) The ESR intensity vs T plot in vacuum, at 1 μW and 10 μW. (b) The corresponding peak-to-peak widths ΔH_{PP} of the ESR signal obtained after fitting the Lorentzian function. Inset of (a) and (b): zoomed-in curves in the range 4-35 K for 1 μW. (c) Inverse static susceptibility as a function of temperature in vacuum (square) and the linear fit (solid line), measured at H=1 T.

suddenly drops by 50 % below 20 K. ΔH_{PP} follows a trend corresponding to the behavior of the intensity. ΔH_{PP} decreases linearly from 6.2 to 2.2 mT upon lowering of the temperature down to 30 K, and suddenly increases by 30 % (0.6 mT) below 20 K. In the elevated microwave power (10 μW) the sudden change in the signal properties becomes a smooth variation as shown in Figs. 1(a) and (b). Unlike the ESR intensity, the static susceptibility does not show any indications of non-Curie behavior down to 2 K as shown in Fig. 1(c). These experimental findings are therefore understood by the presence of a transition from the homogeneous state to an inhomogeneous one at ca.20 K. This is clearly evident in observing a change in the line profile in the vicinity of the transition temperature (T_c ~ 20 K). Figure 2 exhibits the ESR signal at a strong microwave power of 16 mW in the vicinity of T_c. The broadened signal at 10 K shows a slight deviation from the Lorentzian shape indicating an inhomogeneous line-broadening. A prominent hole-burning effect (irregular feature in the ESR signal) appears at 15 K, which is just below T_c, and it is reproducible in repeated runs. The hole-burning feature is an important evidence of serious inhomogeneity appearing in this temperature range. On going

to higher temperatures, hole-burning is gradually suppressed and the line-shape tends to become Lorentzian. Above 25 K the line shape becomes sharpened and purely Lorentzian, exchange/motional narrowing being indicated.

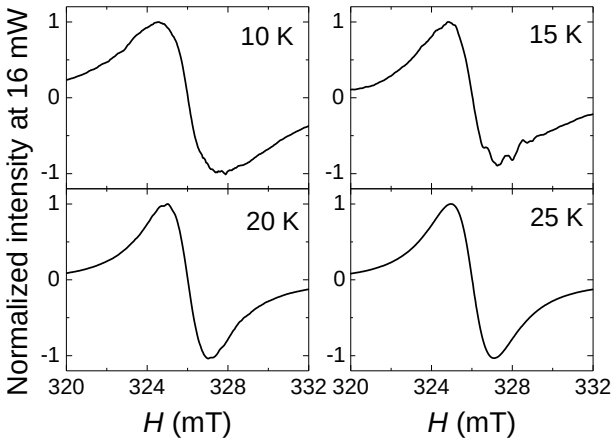

Figure 2. The ESR signals in vacuum at 10, 15, 20, and 25 K measured with 16 mW.

The inhomogeneous behavior below T_c with a discontinuous change in the ESR signal and the appearance of hole-burning phenomenon is a consequence of the presence of a static distribution of on-resonance fields, which indicates the importance of the structural inhomogeneity. Here is a clue in the structure of constituent nanographene sheet in order to explain the structural inhomogeneity. Indeed, each nanographene sheet has its own shape, consisting of arbitrarily positioned zigzag and armchair edges. In an individual nanographene sheet, the compensation of randomly distributed localized spins coupled by ferromagnetic J_0 and ferromagnetic/antiferromagnetic J_1 creates a non-zero net magnetic moment with its own strength. Therefore, the strengths of the ferrimagnetic magnetic moments, which depend on the shape of a nanographene sheet, are randomly distributed in the network of nanographene sheets. This suggests that the on-resonance fields vary inhomogeneously in the ESR signal, depending on the strengths of the magnetic moments of nanographene sheets. The inhomogeneity associated with the distribution of on-resonance fields does not appear in the high temperature range above T_c due to the motional narrowing operated by the fast inter-nanographene-sheet hopping. However, as the temperature is lowered, electron localization develops and nanographene sheets become independent from each other due to the slowdown of electron hopping. Finally, the inhomogeneity survives at lower temperatures below T_c ~ 20 K, where the electron hopping frequency becomes small enough to unveil the inhomogeneous line width. Looking at the experimental finding from another perspective, the observed inhomogeneity reveals a ferrimagnetic feature of individual nanographene sheet, which is predicted from theoretical work [2]. Recent work on magnetic investigations of the ACF samples, in which the inter-nanographene-sheet interaction J_2 is weakened by acid treatment, proves the presence of ferrimagnetic spin fluctuations [8] in good agreement with the present finding, though the apparent Curie-type behavior appears in the present sample due to the presence of weak inter-nanographene-sheet interaction and the absence of magnetic anisotropy as shown in Fig.1(c).

Interestingly, in relation to the inhomogeneous magnetic state, we remind that a spin glass state is created in the vicinity of an insulator-to-metal (IM) transition in the networked nanographene sheets of the ACF sample [6]. In the ACF sample heat-treated below 473 K, the presence of oxygen-including functional groups bonded to edge carbon atoms, which work to block the carriers to hop by weakening the inter-nangraphene-sheet interaction [6,7], results in the formation of Anderson insulator. Heat-treatment above ~1273 K, which can remove the functional groups, enhances the interaction, and further increase in the heat-treatment temperature brings about an insulator-to-metal transition around 1473 K. The spin glass state of the edge-state spins appears in the vicinity of the IM transition. According to the present results, it is considered that the strengthening of the inter-nanographene-sheet interaction induced by the heat-treatment brings the inhomogeneous assembly of relatively independent ferrimagnetic nanographene sheets to a spin glass state in the IM transition region. Then, further strengthening of the interaction well above the transition works to form metallic state at the expense of the edge-state spins.

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